Review

Biofpr Biofuels Bioproducts & Biorefining

Drop-in biofuel production via conventional (lipid/fatty acid) and advanced (biomass) routes. Part I

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Abstract: Drop-in biofuels that are 'functionally identical to petroleum fuels and fully compatible with existing infrastructure' are needed for sectors such as aviation where biofuels such as bioethanol/biodiesel cannot be used. The technologies used to produce drop-in biofuels can be grouped into the four categories: oleochemical, thermochemical, biochemical, and hybrid technologies. Commercial volumes of conventional drop-in biofuels are currently produced through the oleochemical pathway, to make products such as renewable diesel and biojet fuel. However, the cost, sustainability, and availability of the lipid/fatty acid feedstocks are significant challenges that need to be addressed. In the longer-term, it is likely that commercial growth in drop-in biofuels will be based on lignocellulosic feedstocks. However, these technologies have been slow to develop and have been hampered by several techno-economic challenges. For example, the gasification/Fischer-Tropsch (FT) synthesis route suffers from high capital costs and economies of scale difficulties, while the economical production of high quality syngas remains a significant challenge. Although pyrolysis/hydrothermal liquefaction (HTL) based technologies are promising, the upgrading of pyrolysis oils to higher specification fuels has encountered several technical challenges, such as high catalyst cost and short catalyst lifespan. Biochemical routes to drop-in fuels have the advantage of producing single molecules with simple chemistry. However, the high value of these molecules in other markets such as renewable chemical precursors and fragrances will limit their use for fuel. In the near-term, (1–5 years) it is likely that, 'conventional' drop-in biofuels will be produced predominantly via the oleochemical route, due to the relative simplicity and maturity of this pathway. © 2016 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: drop-in biofuels; bioconversion; thermochemical/biochemical conversion; conventional/advanced biofuels; biojet

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Introduction

The vast majority of the 127.1 billion liters of biofuels that were produced in the world in 2014 were either bioethanol or biodiesel (fatty acid methyl esters or FAME).[1] A very small volume of about 4 billion liters of hydrotreated vegetable oils (HVOs) was also produced. Although biofuels only contributed to about 3% of the transportation fuels that were consumed, they played an important role in reducing emissions from transportation, which currently accounts for 14% of the world's total emissions.[2] To be able to keep CO_2 emissions below 450 ppm, the world will need to increase the production and consumption of biofuels significantly, with the International Energy Agency (IEA) projecting that a 27% market penetration of biofuels will be needed by 2050.[1]

The vast majority of the bioethanol that is used today is produced from corn (in the USA) and sugarcane (in Brazil), with smaller volumes produced from wheat, sugarbeet, and cassava in other parts of the world. Bioethanol is a commercially mature and relatively simple technology that involves the fermentation of sugars to ethanol, predominantly using the yeast *Saccharomyces cerevisiae sp*. Although not yet fully commercial, cellulosic ethanol should offer greater sustainability and improved emission reductions. However, only a few commercial-scale cellulosic ethanol facilities have been built in the last few years, with nearly all of them running far below capacity due to various feedstock logistics and technical/engineering challenges. The biomass-to-bioethanol conversion process is more complex, involving pretreatment of the feedstock, the addition of a complex mixture of enzymes which are used to hydrolyze the polymeric carbohydrates to fermentable sugars.

The production of FAME biodiesel uses vegetable oils and fats as the feedstock and involves simple chemistry that can be carried out at a very small scale without any specialized equipment. The triacylglycerides (TAG) in the feedstock are esterified through methanol addition in the presence of an acid or base to form FAME, with glycerol produced as a byproduct. This process is commercially mature and well established (Fig. 1). Unlike ethanol, FAME biodiesel may contain a range of molecules of different hydrocarbon chain lengths. However, the chemistry is the same and all the hydrocarbon chains contain a methyl ester group at the one end (Fig. 2).

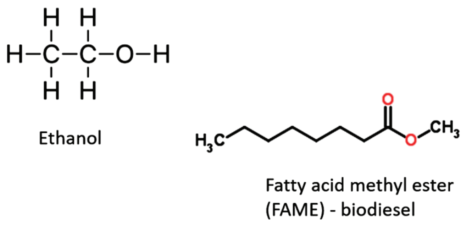

Figure 2. Chemical structure of ethanol and FAME biodiesel.

Globally, the production of conventional bioethanol and FAME biodiesel continues to expand as the conversion processes are relatively simple and commercially mature. However, as these biofuels are mostly based on crops, expansion will likely have limits based on sustainability and food security concerns. Thus, more recent policies in the USA and Europe have tended to gravitate from just supporting conventional (first-generation) biofuels toward incentivizing non-food-based, so-called advanced (second-generation) biofuels, which use biomass/lignocellulosic feedstocks rather than sugars, starch or animal and vegetable oils.

The expanded use of bioethanol and biodiesel will be limited by the fact that they are chemically and functionally distinct from fossil-based transportation fuels. Some of the challenges which limit the increased use of these types of biofuels are; their high oxygen content, which impacts energy density and attracts water; their limited compatibility with existing infrastructure such as vehicles, pipelines, etc. which all contribute to the so-called blend wall; and their complete unsuitability for applications such as aviation.

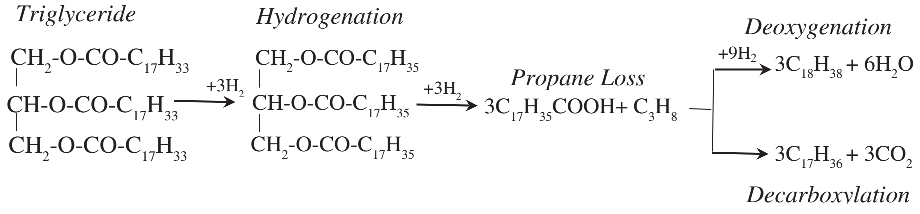

Figure 1. Triacylglyceride (TAG) deoxygenation process.[3]

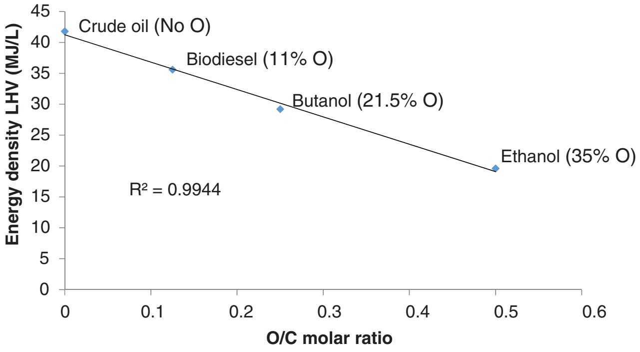

Figure 3. The effect of oxygen content on the energy density of liquid fuels.

The oxygen present in bioethanol and FAME biodiesel accounts for 35% and 11% of the weight of these molecules respectively (Fig. 3). The presence of oxygen reduces the energy density of these biofuels (Fig. 3), subsequently determining the size of a vehicle's fuel tank which in turn influences the travel range for all modes of transportation. Fuel density has a significant impact on the volume and mass of a fuel which, for aviation, impacts minimum take-off weight, thus influencing economics.

The oxygenated functional groups present in bioethanol and FAME biodiesel also means that these fuels are more reactive with refinery and pipeline metallurgy as well as with other biofuel components. The result is the formation of gums, acids and other impurities that are often detrimental to the storability and stability of biofuels.[3,4] The hygroscopic nature of both biofuels results in water adsorption from the atmosphere which contaminates the fuel. It can also encourage the growth of bacteria such as *Acetobacter* which produces acetic acid, leading to corrosion of metal components in pipes and engines. This is a particular problem in older vehicles, two-stroke and marine engines.

Compared to fossil fuels, bioethanol and FAME biodiesel have limited compatibility with the existing petroleum processing and distribution infrastructure and are generally used in low blends. Although higher blends of ethanol can be used in flex-fuel vehicles, this requires a modified engine and fuel system. As infrastructure components, such as vehicle engines, fueling stations, refineries, etc., are very expensive to change, fully compatible, 'drop-in' biofuels could bypass these potential obstacles and facilitate the expansion of biofuel production and use. The majority of the drop-in biofuels that are used today are HVOs. This technology is commercial and relatively mature. Other routes to drop-in biofuels are at various stages of development and they are discussed in more detail below. This, Part I, of the review provides an overview of the technologies to produce drop-in biofuels and some of the technical challenges encountered. Part II will further explore the opportunities to synergize and integrate drop-in biofuel production with existing oil refineries.

Drop-in biofuels

Drop-in biofuels have been defined as 'liquid bio-hydrocarbons that are functionally equivalent to petroleum fuels and are fully compatible with existing petroleum infrastructure',[5] with infrastructure including the engines and turbines where the drop-in fuels are used.

Drop-in biofuels must be functionally equivalent to petroleum fuels (not chemically identical). Functional equivalence is measured by testing the properties of the fuel against specifications such as ASTM standards, for example standards for gasoline, diesel, heavy fuel oil, or jet fuel which have their own specifications for carbon number, boiling point range, freezing point, flash point, aromatic content, etc. Unlike bioethanol, drop-in biofuels generally consist of a mixture of many different types of hydrocarbons and the mixture is characterized by its functional characteristics, such as distillation profile, viscosity, acidity, etc. The carbon number and boiling point range are the parameters that are most commonly used to distinguish between gasoline (light distillates), diesel and jet fuels (middle distillates) (Fig. 4). Gasoline is typically used in spark ignition engines and is comprised of a mixture of C4-C12 hydrocarbons with a 20–40% aromatic content. Diesel is primarily used in compression engines and it contains C10-C22 hydrocarbons with a 25% aromatic content. Aviation fuel is a mixture

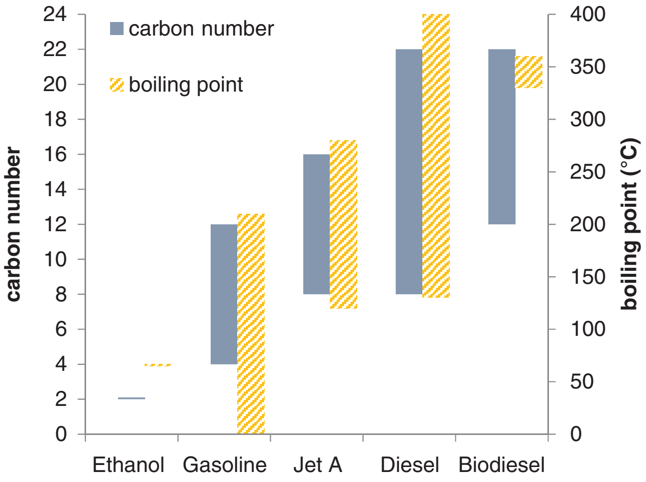

Figure 4. Carbon number and boiling point range of commercial transportation fuels. [6]

of C8-C16 with a maximum of 25% aromatic content. A side-by-side comparison of bioethanol and biodiesel with these fuels highlights their distinct nature (Fig. 4). For specific fuels such as jetfuels, functional equivalence requires compliance with a range of stringent specifications such as very low freezing point (–40°C), thermal stability and low viscosity at low temperatures as described in ASTMD1655 or D7566 or Defstan 91.[6] Although biodiesel has a similar energy density to jet fuel and some overlap in carbon number, it freezes at 0°C, meaning it is unsuitable for aviation applications.

Conversion technologies for producing drop-in biofuels and current commercialization status

Drop-in biofuels can be produced via three main technology platforms, as well as a hybrid category (Fig. 5). Oleochemical technologies, based on lipid feedstocks, can be upgraded to drop-in fuels that are distinct from FAME biodiesel (e.g. hydrotreated essential fatty acids (HEFA) or HVOs. Thermochemical technologies, based on lignocellulosic feedstocks, include gasification or pyrolysis pathways which produce intermediates that can be upgraded to drop-in biofuels (e.g. Fischer-Tropsch (FT) liquids and hydrotreated pyrolysis oils (HPOs)). Thermochemical technologies also include hydrothermal liquefaction and the specific reference to pyrolysis includes all forms of pyrolysis such as fast and catalytic pyrolysis. Biochemical technologies, based on advanced fermentation of sugars derived from conventional feedstocks such as corn or sugarcane, (or cellulosic sugars) typically produce single product hydrocarbons such as farnesene, alcohols or fatty acids that can be further upgraded to drop-in biofuels. Other hybrid technologies incorporate elements of these platforms, e.g. fermentation of off-gases into alcohols which can be upgraded, aqueous phase reforming of sugars and alcohol-to-jet (ATJ) conversion.

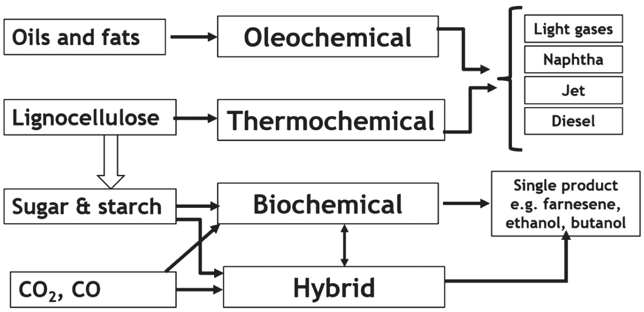

Figure 5. Simplified diagram of different technology routes to drop-in biofuels.

The challenge of removing oxygen in biomass feedstocks to produce drop-in fuels

As discussed earlier, the presence of high levels of oxygen in the fuel is problematic as it lowers energy density and can lead to other problems. However, the feedstocks that are used to produce biofuels, such as sugars, lipids and biomass typically contain high levels of oxygen, up to 40%. Thus, one of the biggest challenges in effectively producing drop-in biofuels is the removal of oxygen from the feedstock.

Deoxygenation is primarily achieved using two main chemical reduction processes, hydrodeoxygenation (HDO) and/or decarboxylation (DCO). Hydrodeoxygenation uses hydrogen to remove oxygen as water (H_2O) while, during decarboxylation, the carboxyl group carbon is oxidized and the oxygen is removed as carbon dioxide. When the DCO approach is used, feedstock carbon is lost by oxidation and, as a result, the overall product yield is reduced. Typically, the addition of hydrogen is preferred when maximal yield is desired. The greater the oxygen content of the feedstock, the more it has to be deoxygenated. This can be determined by calculating the effective hydrogen to carbon ratio of a feedstock.

The effective hydrogen-to-carbon ratio

The hydrogen-to-carbon (H/C) ratio is used in the petroleum and coal industry to indicate how hydrogen rich and energy dense various fossil feedstocks are. This ratio is a reflection of the oxidation state of a molecule and thus the energy that will be released upon combustion. The effective hydrogen to carbon (H_{eff}/C) ratio can be used to reflect the oxygen levels in a potential feedstock. During combustion, the oxygen within the biomass consumes the hydrogen, thus reducing its H_{eff}/C ratio. Thus, using a biomass feedstock where the main elemental components are hydrogen, carbon and oxygen, the H_{eff}/C ratio must account for the relatively high level of oxygen. As each oxygen atom consumes two hydrogen atoms to form a water molecule (H_2O) this contributes no energy to the combustion system.[7] The H_{eff}/C ratio can be used as a rule of thumb and is calculated using the following equation:

$$\mathrm{H_{eff}/C} = \frac{n(H)-2n(O)}{n(C)} \tag{1}$$

where n = number of atoms of each element.

Highly oxygenated and hydrogen-poor feedstocks such as sugar and cellulosic biomass have low H_{eff}/C ratios, for example the H_{eff}/C ratio for glucose is zero. The most common biomass feedstocks and intermediates can be depicted on a 'staircase' which illustrates the extent to which hydrogen inputs will be required to reach the goal of a H_{eff}/C ratio of closer to 2 for a finished fuel (Fig. 6).

As described in Fig. 6, feedstocks such as sugar (used in the biochemical platform) will require the greatest amounts of upgrading (hydrogen inputs), while lipids (e.g. vegetable oil feedstocks used in the oleochemical platform) will require the least upgrading. It should be noted that the staircase and H_{eff}/C is slightly simplified as some types of intermediates, such as ethanol or butanol have a H_{eff}/C of 2, but still require extensive deoxygenation to produce drop-in biofuels.

If we want to produce hydrocarbon molecules from biomass sources, the oxygen will always have to be removed, regardless of whether the conversion technology is oleochemical, thermochemical, or biochemical based. The trade-off between hydrogen inputs and process yields for each of these processes remains unchanged in that the removal of oxygen without hydrogen reduces the carbon in the feedstock and thus the yield of hydrocarbon products.

As currently demonstrated by oil refining, hydrogen can be supplied from an external source, such as the steam reforming of natural gas or other hydrocarbon sources. However, the use of fossil derived external hydrogen will have an impact on drop-in biofuels ability to reduce carbon emissions. In contrast, when the biomass feedstock itself is used as the source of hydrogen, although this should result in lower overall greenhouse gas (GHG) emissions, there will be a loss of carbon and a loss of product yield. It should be noted that hydrogen is required for both deoxygenation and the need to saturate double bonds and increase the overall H_{eff}/C ratio. Hydrogen is also required during hydrocracking to cleave longer chain hydrocarbons into shorter chains of a desired length. Regardless of the conversion technology that is used, hydrogen will be needed for the final polishing and processing of the drop-in fuel.

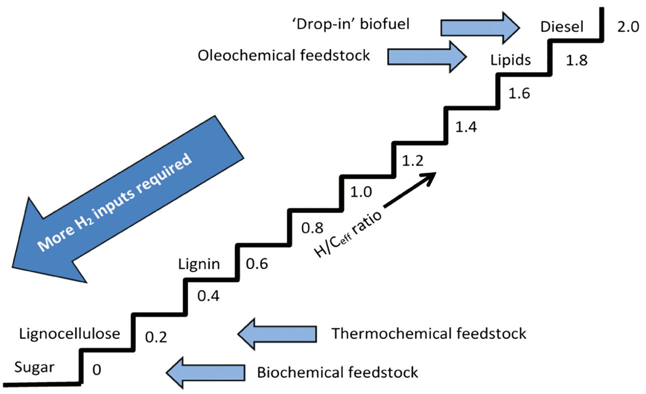

Figure 6. The effective Hydrogen to Carbon ratio 'staircase' for feedstocks.

Oleochemical conversion technologies

The oleochemical route to making drop in biofuels uses oils and fats as feedstocks, upgrading them by the removal of oxygen and then converting them to HVOs or HEFAs. In a standalone facility, HEFA is typically produced in two stages (Fig. 7). During the initial hydrotreatment stage the fatty acids are deoxygenated and double bonds are saturated to create straight-chain alkanes[3]. The second stage involves hydrocracking, to cleave long chain alkanes to shorter chains (if required) and isomerization, which creates branched molecules with improved cold-flow properties. As described earlier, the oxygen in the fatty acids is removed by either the addition of hydrogen (HDO) or due to the loss of carbon (DCO) resulting in the formation of alkyl chains. A combination of the two deoxygenation strategies is typically used in commercial hydrotreating facilities.[3]

A typical HEFA process generates a mixture of products corresponding to light gases (propane and LPG), naphtha, jet, and diesel blendstocks (Fig. 7). The relative amounts of a specific fraction that can be produced in the collective HEFA liquid can be influenced by changing the reaction conditions and catalysts. As fatty acids derived from vegetable oils generally have the majority of their chain lengths in the diesel range, the diesel fraction predominates with only a small portion of the liquids found in the jet range, unless more extensive hydrocracking is carried out.[3,8]

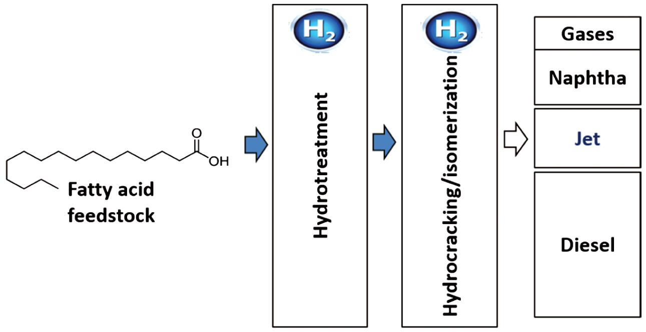

Figure 7. Simplified schematic of the oleochemical conversion process.

However, this also results in a greater amount of gases and naphtha forming as hydrocracking cannot be precisely controlled. Extensive hydrocracking also results in lower overall yields and, importantly, a reduction in the yield of high value products such as renewable diesel. Thus, maximizing jet yield may not the best value proposition unless the jet can be sold at a premium. It is worth noting that naphtha can be converted to gasoline with further processing in a catalytic reformer, or used with light gases to produce hydrogen for use within the facility via steam reforming.

Commercialization status

As mentioned earlier, most commercial drop-in biofuel production to date has been based on the oleochemical platform. The lipid feedstocks contain low amounts of oxygen and have a high hydrogen-to-carbon (H_{eff}/C) ratio (1.8), making them easy to upgrade to drop-in biofuels (Fig. 6). It is highly likely that the oleochemical route will provide the bulk of drop-in biofuel production in the near-to-mid-term while the other technologies are improved. Current annual commercial production capacity of oleochemical derived drop-in biofuels is about 4 billion liters with the majority being renewable diesel or HEFA-diesel with small quantities of HEFA-jet also produced. The current HEFA production facilities (Table 1) predominantly make HEFA-diesel. The exception is AltAir Fuels, which began production in 2016 to make both renewable diesel and HEFA-jet fuels. At this point in time, it is the only dedicated HEFA-jet producer, partly because current policies and economics favor the production of renewable (HEFA) diesel over biojet. It is worth noting that Neste and Boeing have launched an ASTM application for approval of HEFA+ (a term used by Neste, otherwise referred to as green diesel) to be used as an aviation biofuel. HEFA+ is essentially a renewable diesel with good cold-flow properties. Thus, if ASTM approved, the use of HEFA+ could significantly expand the drop-in biofuel available for aviation use, based on existing capacity.

Unlike biofuels such as bioethanol and FAME biodiesel, HEFA production more closely resembles oil refining processes. Not surprisingly, most of the companies that have invested in HEFA commercialization are oil companies (Neste, UOP Honeywell, Valero Energy Corporation, Preem, ENI, Cepsa), with several facilities derived from the repurposing of oil refinery infrastructure (ENI, AltAir Fuels, and Total's proposed conversion of the La Mede Refinery).

Table 1. Current world annual production capacity of HEFA drop-in biofuels.

Company	Feedstock	Billion L/y
Neste (4 facilities)	mixed	2.37
Diamond Green Diesel	tallow	0.49
REG Geismar	tallow	0.27
Preem Petroleum	Tall oil	0.02
UPM biofuels	Tall oil	0.12
ENI (Italy)	Soy & other oils	0.59
Cepsa (Spain 2 demo facilities)	unknown	0.12
AltAir Fuels	mixed	0.14
World Total		**4.12**

Data was obtained from the IEA Bioenergy Task 39 Advanced Demonstration plant database (http://demoplants.bioenergy2020.eu/) Values in metric tons were converted to liters using a density of 0.837 kg/L.

Challenges to expansion of the oleochemical platform

As mentioned earlier, the HEFA conversion route is already commercial and there are few technical opportunities to further optimize this process. The main challenge for this platform is the cost, availability and sustainability of the lipid feedstocks that will be needed to make significant drop-in biofuel volumes.

Most of the lipids that are used for biofuel production are crop-based vegetable oils such as rapeseed, soy, and palm oils. These oils are used extensively in the food sector, raising sustainability and food security concerns, and creating competition for these feedstocks. The price of these feedstocks usually tracks oil prices and vegetable oils are often higher than diesel prices, as indicated when comparing the price of palm oil (Fig. 8), which is the lowest cost vegetable

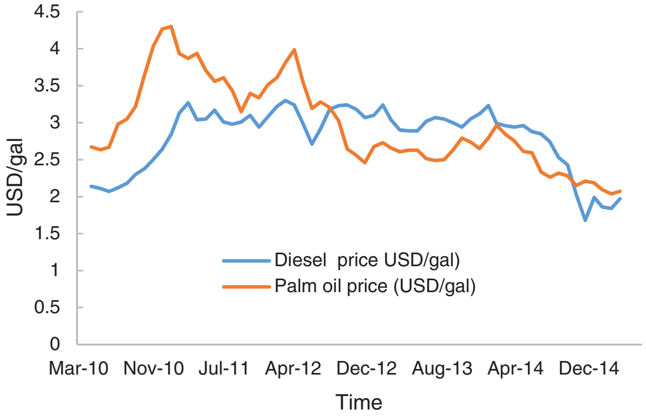

Figure 8. Diesel price versus palm oil price from 2010 to 2015.[9]

oil on the market, with diesel (Fig. 8). For example, in May 2015, palm oil had an average commodity price of \$2.07 USD/gal (\$0.55/L) while at the same time diesel fuel had a price of \$1.87 USD/gal (\$0.49/L).[9] The price of rapeseed oil (canola oil) for the same month was \$2.63/gal (\$0.695/L). As the feedstock constitutes about 80% of the cost of HEFA production, sourcing low-cost feedstock is a priority and is one of the main reasons why companies have tried to maximize the use of low cost feedstocks such as used cooking oil (UCO) or tallow. However, UCO/yellow grease, can also be expensive and, as of July 2016, the price for UCO in the USA was \$25–29/cwt or \$492–570 per metric tonne.[10] To add further complexity, FAME-derived biodiesel and HEFA also compete for the same feedstock, with FAME cheaper to produce, but both receiving the same policy incentives in the USA. It is worth noting that, in the EU, biofuel produced from wastes such as UCO can be double counted to meet that jurisdiction's Renewable Energy Directive.

Partly due to sustainability and food security concerns alternate, supposedly non-edible vegetable oil crops such as camelina and carinata have been proposed as more acceptable oleochemical sources. However, supply chains for these feedstocks have not yet been established and they are currently only available in small volumes. Tall oil, a by-product of the Kraft pulping process has been used to produce drop-in biofuels by UPM and Preem. As there are only limited quantities of Tall oil available (30–50 kg per tonne of pulp) significant expansion based on this feedstock will be limited. It should be noted that Tall oil is already used in several applications and therefore actual availability is not clear. One estimate indicated an availability of <200 000 tonnes crude tall oil in 2013, although production is about 1.5 million tonnes per year).[11] Although production of algal lipids continues to be investigated, they have not, as yet, proven economical. In summary, the greatest challenge for the oleochemical-based route to drop-in biofuels will continue to be the availability of large, commercial volumes of sustainably produced, low-cost feedstocks.

Thermochemical conversion technologies

Thermochemical conversion technologies include the pyrolysis and gasification routes to producing liquid or gaseous intermediates that can be upgraded to drop-in biofuels (Fig. 9). Pyrolysis is conducted at intermediate temperatures of about 500°C, in the absence of oxygen, producing a mixture of gases, char, and liquids (water and water soluble and water insoluble organics, also termed bio-oil). During fast pyrolysis, the residence time is reduced to a couple of seconds or less to maximize liquid yields. Other variations include catalytic pyrolysis and hydrothermal liquefaction. During gasification, the biomass is reacted under pressures of 1–40 bar, typically at temperatures exceeding 800°C, in the presence of regulated amounts of oxygen. Under these conditions gas (synthesis gas or syngas) production is favored, resulting in as much as 85% by mass of the total products.[4] Numerous types of gasification reactors have been used and a good summary can be found in the report by Karatzos *et al.*[5]

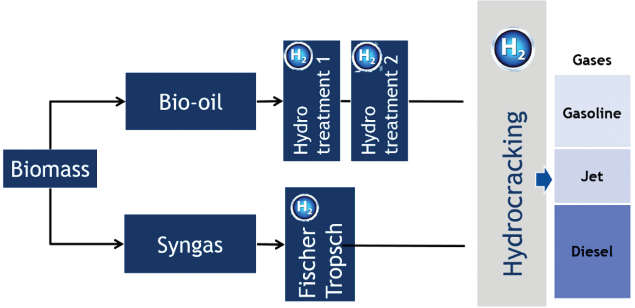

Figure 9. Simplified schematic of thermochemical conversion technologies.

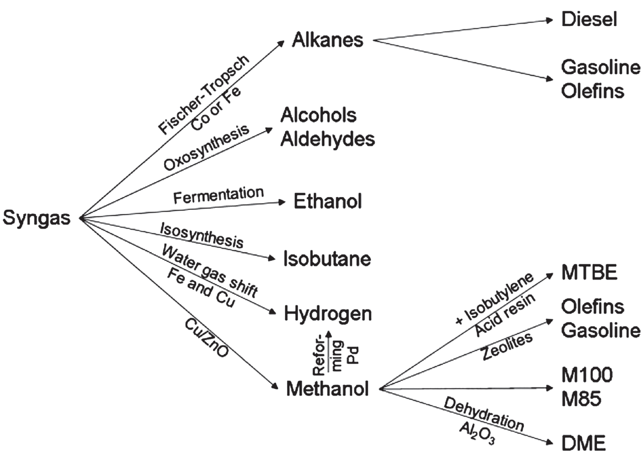

Figure 10. Main syngas conversion pathways.[39]

Both syngas and bio-oil are intermediates that can be used, after limited processing and clean-up, as combustion fuels for stationary power applications such as burners, boilers, furnaces, and industrial kilns. However, drop-in biofuels are more complex and these intermediates have to be catalytically upgraded to oxygen-free hydrocarbons. As described in Fig. 10, upgrading can take various forms such as FT condensation of syngas to produce paraffins or hydrotreatment to produce HPO. To maximize yields, both upgrading technologies require the use of specialized catalysts and as well as hydrogen inputs. The resulting

FT liquids and HPOs are hydrocarbon mixtures that can be further processed via hydrocracking and distillation, resulting in the production of a mixture of gasoline, jet, and diesel range hydrocarbons. In a similar fashion to the oleochemical platform, the proportion of gasoline, diesel, and jet fractions obtained can be adjusted depending on the process conditions.

Although pyrolysis and gasification have many fundamental characteristics in common, the two processes differ markedly in how the biomass intermediates are upgraded, drop-in biofuel yields, capital costs, and hydrogen (H_2) requirements.

Pyrolysis-based conversion routes

The major challenges of upgrading of biocrudes/bio-oils to transport fuels is the deoxygenation of the bio-oil while maintaining high conversion yields and a high H/C ratio in the finished fuel. Typically, the bio-oils obtained after fast pyrolysis of biomass contain up to 40% oxygen. Various bio-oil upgrading strategies have been proposed over the last few decades with the top two contenders being hydrotreating and zeolite cracking.[12] Both processes are catalytic and they selectively promote hydrogenation reactions. However, hydrotreating uses large amounts of hydrogen to remove oxygen from bio-oils in the form of water while, in contrast, zeolite cracking uses no hydrogen but instead rejects oxygen in the form of CO_2, thus lowering product yield. Both technologies try to elevate the effective H/C ratio of bio-oils from about 0.2 to about 2 to fit the functional properties of a hydrocarbon motor fuel. Nearly all the current bio-oil upgrading processes originated in the petroleum industry and use specialized catalysts to improve reaction selectivity.

In most of the hydrotreating processes that have been modelled so far, the biomass to fuel yields are around 25% mass (55% energy) when hydrogen is provided externally and 15% (33%) when hydrogen is produced by gasifying the biomass.[4,13,14] However, as will be described briefly, these relatively poor carbon yields and hydrogen use efficiencies can be improved through the development of more selective catalysts and better optimized processes. The highly heterogeneous, oxygenated, and reactive nature of bio-oils makes their hydrotreatment considerably more complex than that of petroleum. In oil refineries, hydrotreatment is mainly used to remove sulfur from petroleum feeds using catalysts such as sulfided Co-Mo and Ni-Mo supported on porous alumina or aluminosilicate matrices. Unfortunately, for several reasons, these processes are not directly applicable for processing bio-oils and they need to be adjusted. Although precious metals such as Ruthenium, Palladium and Platinum have been assessed as bio-oil hydrotreatment catalysts with encouraging results,[4] the high cost of these metals must be accounted for when developing industrial biofuel upgrading processes.

Upgrading costs have been estimated to account for about two-thirds of the capital expenses and about half the operating expenses of biomass to drop-ins via the pyrolysis route.[15] Although the technical area that would likely have the biggest impact on facilitating improved bio-oil upgrading is increasing the selectivity and lifespan of the hydrotreating catalysts that are used, another key challenge will be to sustainably source the large volumes of hydrogen that will be required.

Gasification and drop-in biofuel synthesis

Gasification is typically conducted under conditions of high temperature and pressure using air, oxygen, or steam as a gasifying agent to convert biomass to a low to medium energy gas known as producer gas or 'syngas'. Unlike raw biomass, syngas is relatively homogeneous and it is comprised of mostly hydrogen and carbon monoxide as well as small amounts of CO_2, H_2O and CH_4. The exact composition of the syngas will vary, partly depending on the composition of the feedstock but mostly on the gasification process conditions that are used. Although syngas can be used for the same applications as natural gas, it is a more oxygenated gaseous fuel with, typically, less than half the energy density of natural gas (natural gas contains about 36 MJ/Nm^3 whereas biomass syngas contains only about 4–18 MJ/Nm^3 (4 MJ/Nm^3 for air blown and 18 MJ/Nm^3 for steam blown gasification).[16] The quality of a syngas for synthesis applications is often measured by its H_2/CO ratio. A higher ratio typically indicates a greater energy density and therefore better potential for upgrading to drop-in biofuels. In contrast to combustion, which results in the conversion of biomass to thermal energy and fully oxidized gases (CO_2 and H_2O), gasification takes place under conditions where oxygen is limited. Therefore, some of the biomass energy is retained in the partially oxidized gaseous product.

The chemical composition of the syngas that is produced depends on the relative prevalence of the reactions taking place during the reduction step of gasification. For example, when adding steam to the reactor, the water-gas-shift (WGS) reaction is favored and more hydrogen is generated, which boosts the H_2/CO ratio of the resulting syngas. Alternatively, when hydrogen is fed to the reactor, the methanation reaction is favored and the generated syngas is rich in CH_4 (useful to produce synthetic natural gas).[17]

The "clean-up" of syngas is one of the key challenges which currently impedes the effective production of drop-in biofuels via the gasification route. Raw biomass syngas is recovered along with impurities such as small char particles, tar vapors as well as volatile nitrogen and sulfur compounds. Char is entrained in the syngas and it is comprised of non-volatilized biomass and ash. The tars that are formed during the polymerization of biomass vapors can stick to the reactor walls and catalysts, resulting in clogging and deactivation. Sulfur and nitrogen gases are derived from the biomass feedstock. These components are deleterious to downstream processes as, upon combustion, they result in the formation of NOx and SOx emissions which can also 'poison' the FT catalysts.[18]

When the syngas is simply burned, these impurities are of lesser concern. However, when the syngas is used for more sophisticated applications such as internal combustion engines, gas turbines and FT synthesis, extensive gas cleanup is essential. Particulates, tars, and acids must all be at concentrations below 50 mg/Nm^3 if the gas is to be used in internal combustion engines. For FT synthesis, the particulate matter must be less than 0.03 mg/Nm^3. Unfortunately, most of the raw syngases that have been produced to date contain contaminant concentrations that typically exceed these limits by several orders of magnitude.

Even if the process is optimized to minimize syngas impurities by adjusting gasification conditions, some clean-up is always needed. Syngas cleanup is one of the most expensive steps of the gasification biofuel platform, typically involving various sequential steps including gas cyclone removal of most of the particulate matter above 10 μm and further removal of the smaller particles by costly methods such as wet scrubbers or electrostatic precipitators.[18] Tars are particularly problematic for FT fuel synthesis as they can irreversibly deactivate the downstream catalysts.

Production of short-chain alcohols from syngas can take place through several routes (Fig. 10). The catalytic condensation syngas pathways that are most relevant to drop-in transport biofuels are the methanol to gasoline and FT processes. However, the FT synthesis pathway is the only direct way to produce jet and diesel range hydrocarbons.

FT synthesis can use syngas derived from many sources including biomass, coal or natural gas and it can produce precursors for a wide range of drop-in chemicals and fuels (Fig. 10). As long as the syngas is treated and conditioned properly and there is a good H_2/CO ratio, functional and chemical equivalence can be achieved with the syngas derived from these disparate feedstocks. However, biomass feedstocks are significantly more challenging to work with. As a result, no commercial-scale biomass-based gasification-FT facility has been built to date. Any drop-in fuels produced via the FT process at commercial scale have all been produced using coal or natural gas as the feedstock.

The final stage of the FT process (Fig. 9) is the hydroprocessing of the resulting hydrocarbon liquids. These FT liquids are essentially oxygen-free such that they can be easily upgraded via hydroprocessing. FT synthesis produces a mixture of hydrocarbon molecules that follow the Anderson-Schulz-Flory distribution. Depending on the catalyst and process conditions used, distribution can favor the gasoline or the diesel range. However, the hydrocracking of long-chain paraffins that is required to produce intermediate hydrocarbon lengths results in a loss of overall yield. Although hydrogen is generally derived from the water-gas shift reaction, this depends on the catalyst that is used as cobalt catalysts do not promote this reaction and hydrogen has to be produced separately.

The capital and operating expenses of gasification-based processes have been estimated by techno-economic analyses to be about double those for pyrolysis.[15] However, this depends on the type of gasification reactor used with plasma gasification producing the cleanest syngas but also proving to be quite expensive. The high capital costs of this platform are due to a variety of factors such as the high operating temperatures, the complexity of the process, multiple process steps and the requirement for various heat-cool and compression cycles. Gas compressors can account for about 18% of total equipment costs and compressor capacity is directly related to process efficiency. Thus, the lower the per pass yield of a process, the more a compressor has to work to recycle the gas stream sufficient times for the gas to react fully.[5]

Pioneering plants have been projected to require double the total project investment cost,[5] with capital costs (TPI) estimated to be in the vicinity of $1 billion for a drop-in gasification plant processing 2000 tpd of biomass (dry basis). Current commercial gasification-FT facilities based on coal or natural gas have had to be very large to achieve the economies of scale necessary to make them viable. However, when using a biomass feedstock, this will be a challenge, as the low energy density of biomass makes it uneconomical to transport over great distances. Although a 5000 tpd biomass-based facility has been suggested as the minimum size that might be viable,[5] this is still 20–25 times smaller than the smallest fossil-based facility.

The insertion of hydrogen into a gasification process differs from a pyrolysis-based process as there is usually minimal-to-no external hydrogen supply required. Although there are exceptions, such as Sundrop Biofuels which uses natural-gas-derived hydrogen inputs, typically the biomass derived syngas itself is the source of the energy and hydrogen needed to reduce and deoxygenate carbohydrates to drop-in biofuel hydrocarbons.

A major advantage of gasification is the perceived, lower technology risk compared to other biofuel platforms as, from a chemical standpoint, syngas is sufficiently similar to commercially upgraded fossil syngas. However, as discussed earlier, biomass syngas is generally of inferior quality and needs extensive clean-up. Tar accumulation, capital costs and scale up challenges have been the main reasons behind the failure of the three, commercial-size start-up, biomass-to-distillates gasification facilities of NSE biofuels, Range Fuels and Choren.[19-22] However, there is still significant potential as new systems and technologies are developed. As the syngas to methanol route is far more forgiving when it comes to syngas quality, gasification-based facilities such as Enerkem have pursued this approach, with other companies producing dimethyl-ether or methane (renewable natural gas) via this route. From a feedstock perspective, lignocellulose feedstocks have the advantage of not generally tracking oil prices the way that vegetable oils and sugar have done (Fig. 11). As the various thermochemical pathways are refined they have the potential for further cost reductions as the processes are optimized.

Current commercialization of thermochemical technologies

The gasification platform for production of fuels is fully commercialized based on coal and natural gas. However, using biomass as a feedstock presents unique challenges and FT synthesis of drop-in fuels have not reached commercial stage, although application of syngas in stationary electricity generation applications is currently taking place in several facilities. Production of FT fuels is planned in proposed facilities in the USA by Fulcrum Bioenergy (based on municipal solid waste) and Red Rock Biofuels (based on forest biomass). Other gasification platforms are currently producing methane, methanol, and dimethyl-ether as biofuels as this approach requires lower capital cost and is less challenging. Biojet fuels produced via the gasification and FT synthesis pathway (FT-SPK and SKA) received ASTM certification in 2009, using coal, natural gas, or biomass as the feedstocks, but no commercial production of biojet based on biomass has yet taken place.

However, pyrolysis-based processes have been used to produce food flavoring (barbeque) and heavy fuel oil for stationary power applications. Recently, the company Ensyn achieved ASTM certification for its products RTPgasoline and RTPdiesel, based on the co-processing of bio-oil in existing refineries.

Although not considered a pyrolysis pathway, hydrothermal liquefaction (HTL) is similar in that it produces a bio-oil that can be upgraded to drop-in biofuel, with the difference that the bio-oil has much lower oxygen levels and is apparently more stable than fast pyrolysis derived bio-oils. Companies such as Licella and Steeper Energy are actively pursuing this technology.

Biochemical conversion technologies

Biochemical conversion to drop-in biofuels typically involves the use of sugar or enzymatically hydrolyzed

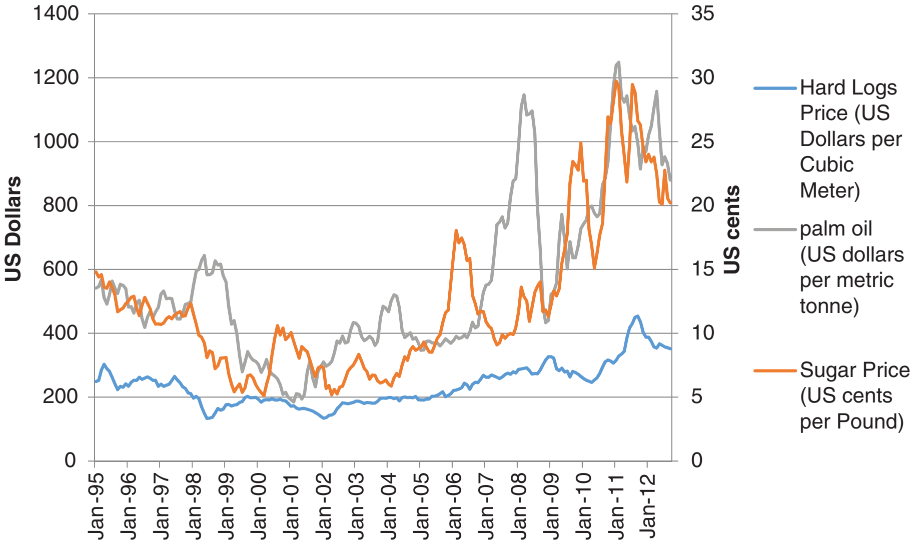

Figure 11. Price fluctuation of food vs cellulosic biofuel feedstocks.

starch or cellulose followed by fermentation lipids, alcohols, or isoprenoids. In the same way that glucose is fermented to ethanol in conventional (or so-called first-generation ethanol production) biofuel production, these advanced biocatalytic processes convert sugars to less oxygenated, more energy-dense molecules such as longer chain alcohols (butanol, butanediol) and higher molecular weight compounds such as isoprenoids and fatty acids. There are numerous biological pathways, feedstocks, and micro-organisms that have been proposed for the production of drop-in biofuels and their intermediates (Fig. 12).

Micro-organisms such as cyanobacteria and algae can also directly capture CO_2 from the atmosphere and convert it to ethanol or lipids. Alternatively, bacteria, yeasts, and heterotrophic algae can utilize sugars derived from sugarcane, sugarbeet, starch, and other energy storage polysaccharides, or from the hydrolysis of the cellulose and hemicellulose carbohydrates in cellulosic biomass. Although other bacteria can utilize hydrogen and carbon monoxide in syngas this is discussed in the subsequent hybrid technologies section. Although the various intermediates can be used for diesel or gasoline production, the more oxygenated higher alcohols are predisposed for subsequent gasoline production while the higher molecular weight, longer chain more saturated lipids and isoprenoids are better suited for diesel and jet fuel production. Cyanobacteria, yeasts, and bacteria can be selected or engineered to produce either higher alcohols or isoprenoids and lipids with the potential that the metabolic pathways from one micro-organism can be heterologously expressed in another. However, after biological production, regardless of which biosynthesis route is used, some form of hydroprocessing of the produced intermediate will typically be required to produce a drop-in biofuel. As discussed earlier, the more oxygenated and unsaturated the intermediate, the more hydrogen is required for it to be upgraded to a fungible drop-in functional equivalent to diesel, jet, or gasoline blendstock. From a commercialization point of view, one of the most attractive characteristics of these technologies is the potential to piggy-back on existing ethanol facilities by switching the micro-organisms used in the fermentation process to a ‘microbe-to-drop-in fuel or fuel intermediate’ process.

There are four main metabolic pathways that have been proposed for the conversion of glucose to the chemically reduced molecules that could constitute drop-in biofuels

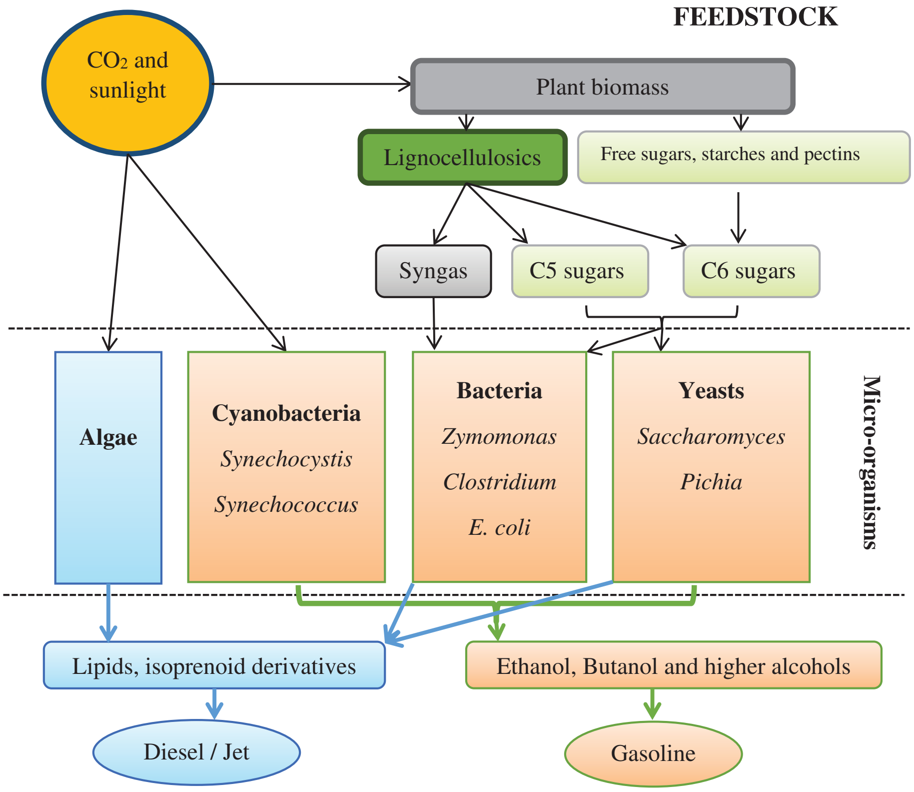

Figure 12. Schematic overview of the micro-organism-to-drop-in-intermediate or biofuel derived for various renewable feedstocks. Adapted from Weber *et al.*[31]

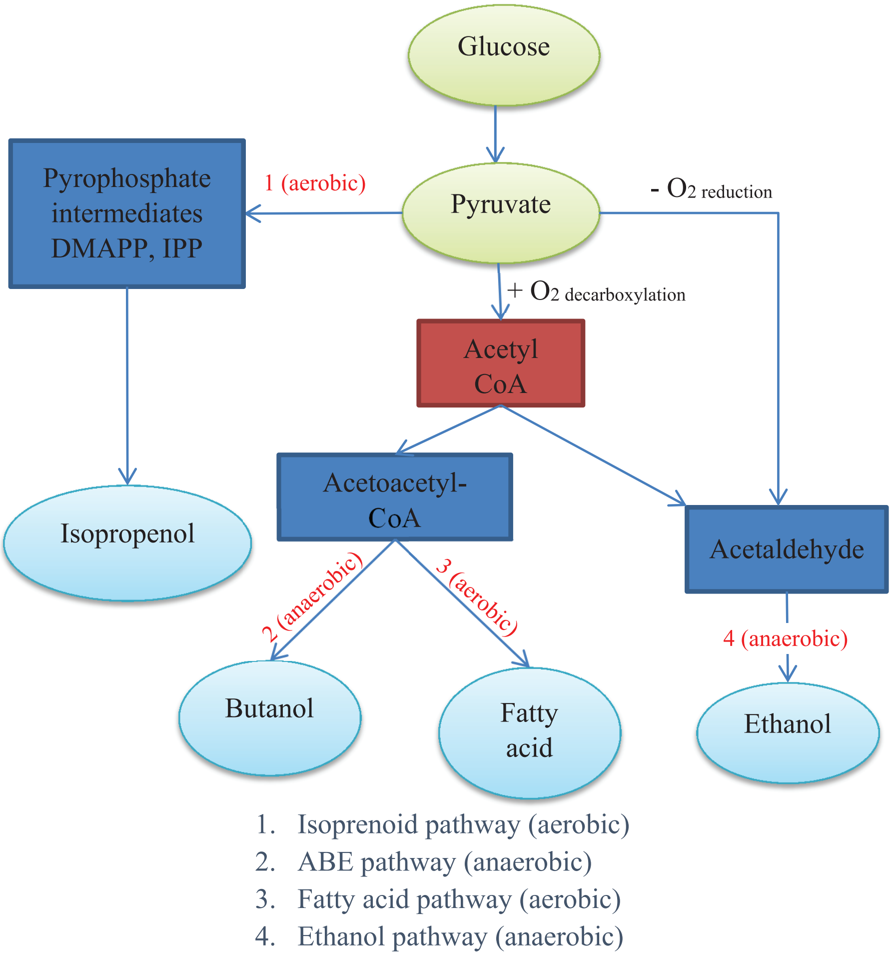

Figure 13. Simplified schematic of major metabolic pathways relevant to drop-in biofuel production.

(Fig. 13). All the pathways begin with the oxidation of glucose to two pyruvate molecules (glycolysis). From there the pathways differ as the pyruvate is converted to various intermediates such as Acetyl CoA or acetaldehyde. The pathways that lead to butanol and alcohol are anaerobic whereas the pathways that lead to more saturated longer chain molecules such as isoprenoids or fatty acids are aerobic.[23] Each pathway plays a different role in the production of drop-in biofuels in terms of productivity and suitability for drop-in biofuel production.

As can be seen when the specific pathway for biosynthesis of the fatty acid, palmitate, is used as an example (Fig. 14), each elongation cycle expends the reducing power of two NAPDH molecules. Regenerating the NADP+ to NADPH typically requires a portion of feedstock carbon to be oxidized to CO_2 and H_2O via aerobic respiration.[24] The NADPH generation process takes place within the pentose phosphate pathway (PPP) and the reducing power of NADPH essentially provides the means of hydrogen insertion.

Inserting molecular hydrogen via alternative means has been shown to increase yields (and decrease the need for carbon-consuming NADPH generation) in metabolic processes involving chemical reduction of carbohydrates.[25] The longer and more saturated the fatty acid chain, the more elongation cycles and greater reducing power required. This reducing power has to come from either alternative hydrogen inputs or from oxidation of feedstock carbon which sacrifices yield.

The commercial viability of the biochemical platform is primarily influenced by biological conversion performance and efficiency and the amount of process inputs (e.g. nutrients, process energy, and equipment) required to produce and recover the target molecules from the production broth. As sugar feedstocks are relatively costly, to achieve good process economy the biofuel (or biofuel intermediate)

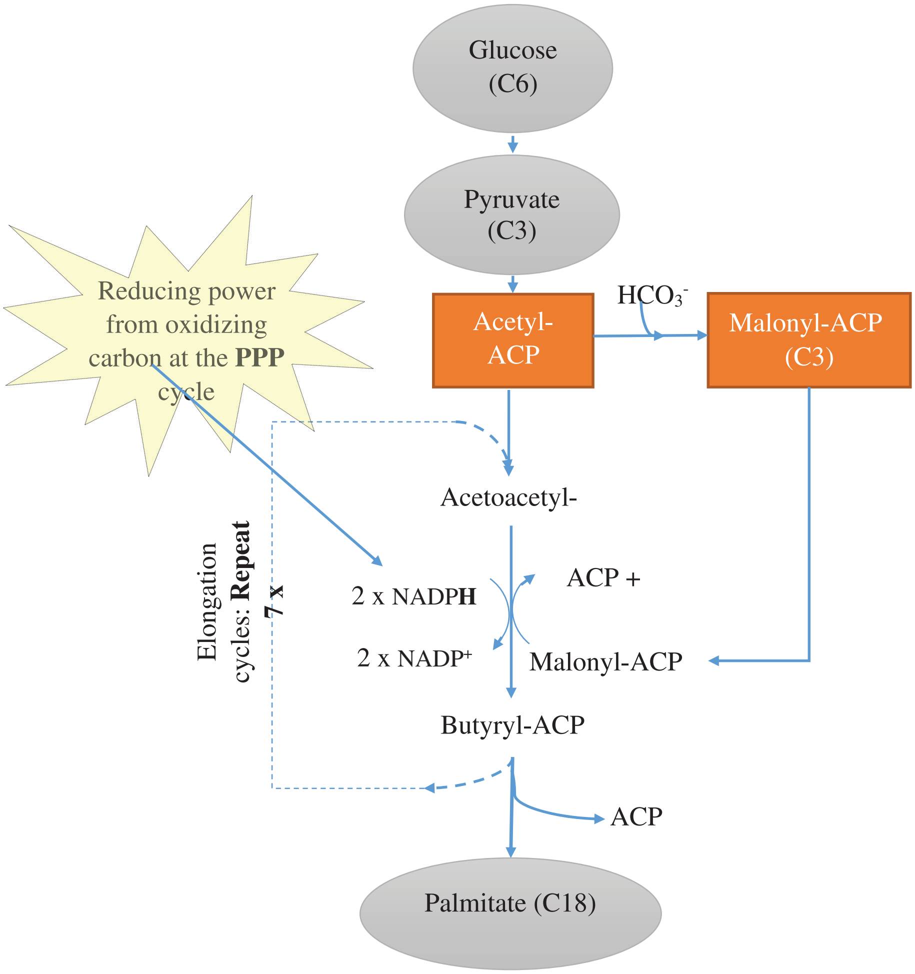

Figure 14. Biosynthesis of fatty acid, palmitate clearly illustrating the addition of hydrogen from NADPH. A total of 14 hydrogen atoms are required and this reducing power is acquired form oxidizing of carbon at the PPP. Adapted from Jovanovic Tews *et al.* [24]

production and recovery process steps must be highly efficient and robust to achieve the type of performance that can be achieved by the 'gold standard' of the established sugar-to-ethanol fermentation processes. However, in comparison the alternative drop-in biological processes are more energy and carbon intensive and achieve much lower productivities than the conventional sugar-to-ethanol fermentation processes. For example, ethanol production using *Saccharomyces cerevisiae* can typically achieve volumetric productivity of 2.00–3.00 g/L/h, butanol production using *Clostridium* spp. can only achieve 0.08–0.46 g/L/h while farnesene productivity is about 0.70 g/L/h.[5]

A significant degree of technological uncertainty and risk remains in biological processes for producing drop-in biofuel-relevant molecules, especially when genetic engineering of the production micro-organisms is involved. The lipids and solvent-type molecules that are used as precursors for drop-in blendstocks are usually secondary metabolites which are not directly associated with cellular energy metabolism but rather with cell growth, maintenance, and survival. They are typically only produced in small amounts unless the micro-organism is stressed. Another challenge is that, when larger amounts of these types of products are produced, it is usually at the expense of cell growth. For example, algae typically produce higher yields of lipids when they are nitrogen starved and, consequently, are limited in carrying out the protein synthesis needed for growth.[26] From a microbe survival standpoint, saturated compounds like lipids are accumulated in non-growing cells as a means of storing energy to protect the organism against potential future energy limitations.[24,26] There is also usually a lag in the time between the initiation of the biological process and the onset of accumulation of secondary metabolites such as lipids. In contrast, ethanol production by yeast (or bacteria) occurs by a central metabolic pathway linked to primary energy metabolism.[27] Consequently, fermentative ethanol production is directly associated with cell growth and there is no time lag in ethanol production after the process is initiated.

The industrial robustness of the various microbial strains and the ease of scale-up of biological-based production processes will have a significant influence on how quickly advanced biological processes for drop-in-relevant products can be successfully commercialized. It should also be noted that the industrial challenges differ significantly for aerobic (isoprenoid and fatty acid) and anaerobic processes (n-butanol and isobutanol). However, the biochemical-based platforms have a distinct advantage over the thermochemical processes in the production of renewable chemicals in that they can be produced at high selectivities. Although, the lower volumetric productivities and yields of these still evolving microbially derived industrial processes might prove challenging when trying to achieve cost competitive biofuel production, their use as higher-value chemical feedstocks has proven to be profitable. The lower yields and different chemical characteristics, as compared to ethanol, have been shown to require different innovative approaches in the recovery of the product from the aqueous broth. As the final product titer is strongly associated with process capital and operating costs, lower titers typically mean the need for more production vessels (or volume) to produce a given quantity of product while greater amounts of process energy might be required to recover a given amount of product. Thus, it is unlikely that most biochemically derived products will be used as drop-in biofuels before these higher value chemical, cosmetic, pharmaceutical, etc., markets are saturated. For example, normal butanol typically commands a price of about USD $5.00/gal or $1.32/L,[28] as a commodity chemical versus US $2.25/gal or $0.60/L (based on USD $2.9/gal & 36 MJ/L gasoline and 28 MJ/L butanol) as a gasoline energy equivalent. As the chain length of these biochemically derived products gets longer, even more valuable applications are possible, (e.g. Amyris' farnesene which commands higher prices in the cosmetics/detergent markets).

It should be noted that the biochemical platforms are more efficient and suitable for producing oxidized products than highly reduced molecules. Highly oxidized products such as lactic, acetic and adipic acids command significantly higher prices than ethanol or biodiesel and they are difficult to make via the non-biochemical platforms. Since sugar molecules inherently contain high amounts of oxygen, it is likely more economically attractive to convert them to oxidized intermediates than to drop-in hydrocarbon fuels. In the near term, market saturation issues for renewable chemical products should not be a concern due to projected strong growth in bio-based material markets.

In summary, in contrast to the oleochemical and thermochemical platforms, the biochemical approach to making drop-ins results in the production of 'pure' molecular streams of functionalized molecules which currently command higher chemical market prices than as intermediates for drop-in biofuels. The primary role of the metabolic pathways involved in drop-in biofuel production is to biologically deoxygenate the sugar feedstock (low H_{eff}/C) to produce more highly reduced or saturated products such as isoprenoids and fatty acids (high H_{eff}/C). However, these biological processes are comparatively energy and carbon intensive and achieve productivities considerably lower than conventional sugar-to-ethanol fermentation processes. In the near-to-mid-term demand for biochemical drop-in products is expected to grow and remain significant as markets for bio-based chemicals continue to expand.

Commercialization status of biochemical platform drop-in biofuels

Several companies are trying to commercialize biochemical-based drop-in technologies. For example, Amyris is producing farnesene at a commercial scale and this intermediate can be hydrotreated to form farnesane which has been ASTM approved for use as a biojet in blends of up to 10%. Although this drop-in biojet fuel has been used by airlines such as Cathay, it is probable that the main focus of the company will be the development of chemicals for markets such as cosmetics or as degreasing agents, as these are a higher value propositions. Similarly, although Gevo's isobutanol technology platform has been used to make alcohol-to-jet, isobutanol is a valuable chemical intermediate that is currently used by companies such as Coca-Cola to produce its Plantbottle™.

Hybrid conversion technology platforms

Although most drop-in biofuel technologies are captured under one of the previously described oleochemical, thermochemical or biochemical platforms, some technologies combine two or more of the platforms described earlier and are therefore referred to as 'hybrid' routes to drop-in biofuels. The main approaches within the category are syngas fermentation, aqueous phase reforming, and ATJ.

Syngas fermentation

As described previously, the conversion of syngas to liquid biofuels can be achieved thermo-catalytically. However, some fermentative micro-organisms can also utilize syngas as their carbon and energy source to produce potential drop-in biofuel intermediates. Some autotrophic micro-organisms can use single carbon compounds such as CO and CO_2 as sources of carbon and energy-rich compounds such as CO and H_2 as sources of energy. Micro-organisms such as *Clostridium ljungdahlii* and *Clostridium carboxidivorans* can ferment syngas to intermediates such as ethanol, butanol, and acetic acid.[29] These micro-organisms use the *Wood-Ljungdahl* pathway (Fig. 12) to reduce CO to Acetyl-CoA, from which ethanol and butanol are produced. The reducing power required for the first reaction comes from the H_2 in the syngas or from the oxidation of CO to CO_2 via a carbon monoxide dehydrogenase enzyme.[30,31]

Syngas fermentation is claimed to have several advantages compared to alternative processes, i.e., sugar fermentation and thermocatalytic syngas conversion.[29,30] For example, compared to sugar fermentation, this approach can utilize lignin in addition to carbohydrate fractions of biomass. In comparison to thermocatalytic syngas conversion claims have been made that it is more economical at a smaller scale, because of lower capital costs, while proving to be less sensitive to impurities.[30] However, the volumetric productivity of the hybrid approach is still quite low, with current volumetric productivities around 0.3 g/L/h, similar to the biochemical routes to butanol and farnesene. It appears that the primary limiting step for syngas fermentation is the low solubility of CO and H_2 gases in aqueous solutions, as these gases must first be absorbed into the aqueous fermentation broth to be microbially assimilated.[32] As the gas-liquid mass transfer and solubility of both molecular hydrogen and carbon monoxide in water are quite low, compared to more conventional sugar substrates (where gas-liquid mass transfer is not needed), syngas fermentation rates are typically constrained by physical mass transfer limitations rather than being limited by metabolic capacities.

From an energy balance perspective, the syngas has to be cooled down from a production temperature of ca. 700°C or higher to ca. 50°C or less before it can be fermented. This significant cooling requirement could be problematic as the temperature fluctuations that are commonly encountered in gasification systems result in significant engineering challenges and generally have an adverse effect on process energy efficiency.

INEOS Bio and LanzaTech have built and are operating large demonstration/small commercial- scale facilities using syngas fermentation technology. However, ethanol has been the main product to date, not drop-in biofuels.

Aqueous phase reforming

The thermochemical catalytic conversion of biochemical platform-produced sugars to hydrocarbon biofuels has been termed aqueous phase reforming (APR) and Virent Energy Systems (Virent) is the highest profile company currently trying to commercialize this approach.

This technology is classified as a hybrid as it converts sugars, (nominally biochemically derived from starch/biomass), to drop-in biofuels using a thermochemical catalytic process. Variations of APR also have been used to produce hydrogen from the aqueous residues of pyrolysis oil separation and upgrading processes.[4] Earlier work showed that highly reduced carbon molecules could be produced when sugars (or other polyols) in aqueous solution were mixed with molecular hydrogen and passed over ZSM-5 catalysts.[33-35] This initial work ultimately lead to the creation of Virent and the development of its patented BioForming^{TM} process, which comprises a combination of the original APR process combined with upgrading technologies used in oil refineries. The process uses heterogeneous catalysts operating at moderate temperatures (175 to 300°C) and pressures (10 to 90 bar) to reduce the oxygen content of the (plant biomass derived) sugar or polyol feedstock through the three main steps described:[21,35,36]

- Acid-catalyzed dehydration of sugars.
- Aldol condensation of dehydrated carbohydrates over solid base catalysts to form large organic molecules.
- Dehydration/dehydrogenation of the large organic molecules to alkanes using bifunctional catalysts (this step represents a variation of conventional catalytic processing as found in petroleum refineries).

The Virent process yields a product that has similar properties to petroleum reformate, although the exact mixture composition depends on the nature of the catalysts and reaction conditions used. Acidic catalysts such aluminosilicates (e.g. ZSM-5) favor the production of shorter molecules of a more phenolic nature (more suitable for gasoline blends) while base catalysts favor chain elongation through aldol condensation, thus forming longer chain liquid products (more suitable for diesel blends).[36] Noble metal catalysts such as Pt and Rh favor reforming of carbohydrates to hydrogen and CO_2.[37] The reformate can then be upgraded to a drop-in biofuel using conventional refinery processes. The process consumes 12 wt% (of dry feedstock) hydrogen, some of which is produced via the APR process itself.

The APR approach is attractive because it has the potential to be used to produce highly reduced (high H_{eff}/C) hydrocarbons from a diversity of water soluble organic carbon compounds including both C5 and C6 carbohydrates at much faster reaction rates than are possible using biochemical routes (e.g. residence times of minutes vs hours or days). However, the APR reactions are less selective than fermentation processes and produce a complex mixture of organic molecules. Although the APR process uses non-exotic process components and catalysts, it faces catalyst coking and deactivation challenges similar to those encountered during the upgrading of pyrolysis oils. During the catalytic upgrading of water soluble saccharides and bio-oil fractions, catalyst coking and deactivation have been shown to increase with decreasing feedstock H_{eff}/C ratio. Consequently, feedstocks with an H_{eff}/C effective ratio less than 0.15 have been shown to cause large amounts of coke formation (more than 12 wt%) from homogeneous decomposition reactions [38]. Given that sugars have a H_{eff}/C effective ratio of 0, if coking problems can be avoided through effective catalyst regeneration, this will significantly enhance the likely commercialization of the aqueous phase reforming route to drop-ins.

Alcohol-to-jet

The thermochemical catalytic conversion of biochemically produced alcohols (e.g. ethanol or butanol) to hydrocarbon biofuels is also known as the ATJ process. Companies such as Gevo, BYOGY, and Cobalt are pursuing this approach. Although ATJ and acid-to-alcohol technologies are technically proven, as mentioned earlier, the intermediates are typically more valuable as renewable chemicals than as jet or alcohol fuels. Isobutanol-to-jet received ASTM certification in early 2016 and ethanol-to-jet should also obtain certification in the near future. It is possible that alcohol-to-jet could become more commercially attractive in countries such as Brazil and the US where ethanol is available at relatively low cost, or where the blend wall constrains expansion of ethanol as a gasoline blend.

The ATJ process is relatively simple, resembling the methanol to gasoline process (Fig. 10). The main processes have been performed in the chemical and fuel industries for decades and involve dehydration, oligomerization, and hydrogenation. Although the technology risk is low this approach is economically challenging as it is energy intensive, involving highly exothermic reactions. Similarly, experiences gained in establishing methanol-to-gasoline processes have shown that alcohol-to hydrocarbon reactions are difficult to scale up due to the requirement for multiple reactors and extensive heat exchanger installations, although the exothermic heat of reaction for ethanol-to-gasoline conversion is smaller than that of methanol to gasoline. A major challenge is that the final drop-in product might command a lower price than the feedstock alcohol.

Conclusions

Drop-in biofuels are functionally equivalent to petroleum fuels and are fully compatible with the existing petrochemical infrastructure, including the fuels distribution and the engines in which they will be used. Their development will be important for industries such as aviation where no other alternative currently exists. Although there are several technology routes to drop-in biofuels a major challenge for all the routes is the high oxygen content of biomass feedstocks and the need for effective oxygen removal to create typical hydrocarbon fuels. The effective-hydrogen-to-carbon-staircase is a useful tool that uses the oxygen content of feedstocks to project the likely difficulty in upgrading them to drop-in biofuels. Lipids have the lowest oxygen content (11%) and the highest H_{eff}/C ratio, thus providing the simplest (requiring the least processing) route to drop-in biofuels. As a result, the oleochemical derived process is the only one producing commercial volumes of drop-in biofuels (HEFA) at this time. It should be noted that conventional biojet, produced via the oleochemical route, will have to grow substantially to establish the market and supply chain so that advanced biojet, derived from biomass substrates, has time to prove to be technically, economically and sustainably more competitive.

The main challenges that must be addressed to encourage further HEFA production relate to the availability, cost and sustainability of the feedstock. Lipid feedstocks (such as vegetable oils) are expensive and come with potential sustainability challenges such as land use change and competition with food markets. Virgin vegetable oils have historically been priced higher than diesel fuel for long periods of time. Although alternative lipid feedstocks such as used cooking oil and tallow are typically cheaper and more sustainable, they are limited quantity. However, in the near-to-mid-term, the HEFA process will continue to supply most of the commercial volumes of drop-in biofuels.

In time, thermochemically derived processes, using lignocellulosic feedstocks which should be more abundant and less costly than lipids, will likely become the major supplier of drop-in biofuels. However, there are significant technology challenges that have still to be resolved. Although gasification is an established technology, the FT synthesis of drop-in biofuels continues to encounter problems with syngas quality and clean up. Additional challenges include high capital costs and the need to operate large-scale facilities will mean that the logistics involved in handling large amounts of a low-density feedstock such as biomass will have to be resolved. The pyrolysis/hydrothermal liquefaction approaches to making bio-oils/biocrudes have considerable potential as they can effectively utilize a range of biomass feedstocks and they have relatively low capital costs as compared to gasification. However, a pyrolysis approach has high hydrogen requirements while upgrading the biocrude to a high-specification fuel is hampered by the cost and short lifespan of the required catalysts. Although the biochemical route to drop-ins provides single products with defined chemistry, which can be readily upgraded to biofuels, these intermediates are often more valuable in biochemical/bioproducts markets and are thus too valuable to use as a biojet fuel feedstock. Until these markets are saturated, it is unlikely that these products will be used to make biofuels.

Regardless of the production platform, the major interconnected parameters that will influence the rate of commercialization of drop-in biofuels are capital and operating expenditures, process yields and productivities and feedstock sourcing. Each approach is and will encounter different degrees of sensitivity to each of these parameters.

Sustainably derived hydrogen will play an important role in the conversion of biomass to drop-in fuels, based on the effective H/C ratio and the requirement for extensive oxygen removal from biomass. Although hydrogen sourcing and cost improvements can potentially be achieved based on synergies with the existing oil refining industry, it is likely that this will be fossil-derived hydrogen in the short-to-mid-term. However, co-location and co-processing of drop-in biofuel production with oil refineries are two key options that should be better explored. Drop-in biofuel production more closely resembles oil refining processes, rather than biological fermentation. Thus, it is likely that the knowledge, experience, and potentially infrastructure of the petrochemical sector can be exploited to the benefit of drop-in biofuel production and expansion. This will be further explored in Part II of this review.

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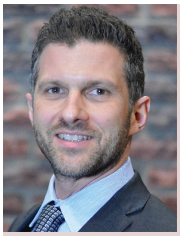

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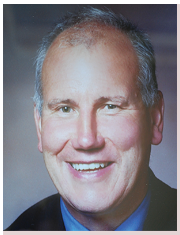

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